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Research on Optical Properties and Micro-processing Characteristics of Collodion Thin Film

Chang-long CAI*, Xiong HAN, Xiao-ling NIU, Wei-guo LIU

Micro-Optoelectrical System Laboratory, Xi'an Technological University, Xi'an 710032, China

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Abstract

Colorless and transparent thin films of collodion are prepared on silicon wafers and K9 optical glass substrates by using spin-coating technique. The visible light transmittance, IR absorption spectra and optical constants of collodion thin film are measured by UV-3501 Spectrophotometer, Fourier transform infrared spectrometer (FTIR) and spectroscopic ellipsometry. The measured results show that its average visible light transmittance is 91.9%, and its average infrared absorptivity is better than 0.69/ μm . In the visible light region, the refractive index of collodion thin film changes in the range of 1.5–1.53, which accords with normal dispersion. The collodion films are etched using oxygen gas plasma. The surface morphology and thickness of etched thin film are measured by the polarizing microscope and MP-100S thickness measurement system, respectively. The results show that the collodion thin film is etched out in the oxygen gas plasma.

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Keywords: Collodion thin film; Transmittance; Infrared absorptivity; Micro-processing

1. Introduction

In recent years, with the development of uncooled infrared detectors, a new uncooled infrared detector with optical readout mode appeared [1,2]. However, the infrared radiation absorption of optical readout infrared detector is unsatisfactory. In order to improve the detectors' response to infrared radiation and not affect the readout of light signal, it is necessary to prepare a layer of thin film which is transparent to visible light and has high infrared absorptivity on the detection unit.

The commercial name of collodion is called nitrocellulose, collodion solution or gun cotton. Collodion is derived from concentrated nitric acid and concentrated sulfuric acid acting on absorbent cotton, which is flammable, and freely dissolves in purified alcohol, ether and acetone. Collodion solution is highly volatile. Dense films formed after volatilizing does not dissolve in water, which can be used to manufacture varnish, bonding paste, photographic film, artificial pearl, and artificial leather, and often used as the tissular embedding and tablets in the histology [3,4]. The collodion is not expensive, easy to fabricate, and has many advantages in the application of photoelectric devices. The collodion thin film is often used as the infrared absorptive material in infrared sensor [5], which can improve the sensitivity of the device.

The preparation of collodion film is unique. Wang et al. [6] reported that the collodion acetate amyl fat solution is dripped into the distilled water to prepare the collodion thin film. But the uniformity of collodion thin film prepared using this technique is bad, and its thickness is not easy to control. However, these disadvantages can be conquered by means of

* Corresponding author.

E-mail address: changlongcai@126.com (C.L. CAI).

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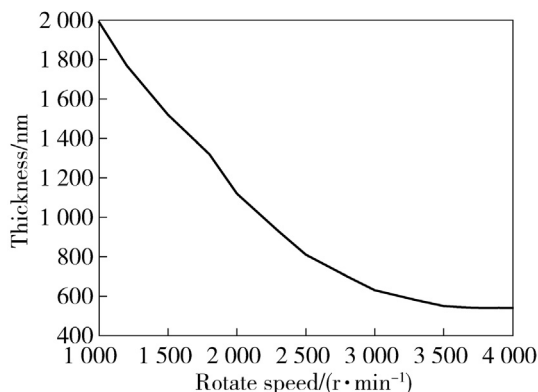


Fig. 1. Relationship between thickness of collodion thin film and rotating speed of spin coater.

spin-coating method, and the collodion films meet the requirement of high visible light transmittance and infrared absorption.

2. Optical properties of collodion thin films

2.1. Growth characteristics of collodion thin films

The collodion solution produced by Tianjin Hengxin Chemical Preparation Co., Ltd is used as the experimental materials, and the silicon wafers is used as substrates. The substrates are cleaned by ether, absolute ethyl alcohol, ultrasonic wave, deionized water and high purity nitrogen one after another. The cleaned substrate is put on the center of turnplate of KW-4A table type spin-coater developed by Institute of Microelectronics of Chinese Academy of Sciences. If a moderate collodion solution is dripped on a silicon wafer, a layer of thin and uniform film is formed on it under the action of centrifugal force and surface tension of liquid by spin-coating method [7]. The thickness of collodion thin film could be controlled by changing the parameters of rotating speed and time. The relations between the rotating speed of spin coater and the thickness of collodion thin film were acquired by a number of technological experiments, as shown in Fig. 1. It can be seen from Fig. 1 that the rotating speed decreases with the increase of thickness. The thickness of collodion film no longer varies when spin-coating speed is more than 3500 r/min, this can be explained by the concentration and volatileness of collodion solution. More thinner thin films can be prepared by using dilute collodion solution.

Three groups of collodion thin films were prepared by spin-coating technique with the rotating speed 1800 r/min and the spin coating time of 12 s. The thickness of collodion thin films was measured by MP-100S imported from the United States.

Table 1
Thickness of collodion thin films

Random point	1	2	3	4	5
No. 1	1322 nm	1321 nm	1323 nm	1322 nm	1324 nm
No. 2	1321 nm	1321 nm	1323 nm	1324 nm	1323 nm
No. 3	1320 nm	1322 nm	1324 nm	1325 nm	1323 nm

Five points of each sample wafer were measured randomly, and the fit value is less than 1. The final thickness is the average thickness listed in Table 1.

It can be seen from Table 1 that the thicknesses of thin films have little difference among them, higher uniformity and good repeatability. This technique provides us a good method to fabricate collodion thin films.

2.2. Transmittance of collodion thin film

The test sample wafer is prepared by using the KW-4A desk type spin-coater. The optical glass K9 with the thick of 1 mm and the diameter of 20 mm is used as substrate, and the preparation parameters are the rotating speed of 1800 r/min and the spin coating time of 12 s. The thickness of collodion thin film sample is 1320 nm. Hitachi U-3501 Spectrophotometer is used to measure the transmittance of collodion thin film in the range of 380–760 nm, and the measuring step length is 2 nm. The results are shown in Fig. 2.

It can be seen from Fig. 2 that the minimum transmittance is 91.2% and the maximum transmission is 92.3%. The average transmittance of collodion thin film in the visible light region is about 91.9%.

2.3. Infrared absorption spectrum test

Double-sided polishing silicon wafer of which resistivity is about 5–9 Ω cm is used as substrate of test sample. The substrate is treated in standard cleaning technique and dried before preparing collodion thin films. The spin coating parameters are the rotating speed of 1800 r/min, the rotating time of 12 s. The thickness of collodion thin film is about 1320 nm. The infrared absorption spectrum is acquired by using American Perkin–Elmer Fourier transform infrared spectrometer. The infrared absorption spectrum is shown in Fig. 3.

It can be seen from Fig. 3 that the average infrared absorptivity is better than $0.69/\mu\text{m}$ in wave number of 3333–2000 which is the atmospheric window of 3–5 μm . This means that the light intensity is reduced to 1/3 of initial light intensity after the light propagates 1.44 μm in the collodion thin film [8]. There exit some absorption peaks exit

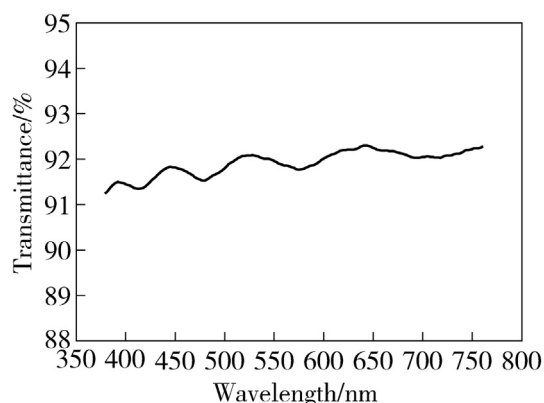


Fig. 2. Transmittance of collodion films in visible light region.

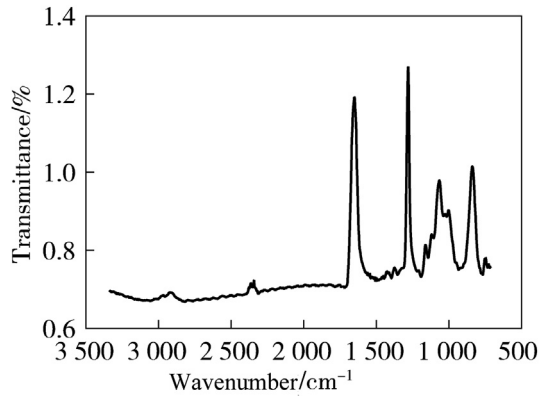


Fig. 3. The infrared absorption spectrum of collodion film.

in the wave number of $1750\text{--}715\text{ cm}^{-1}$, which include the infrared window of $8\text{--}12\text{ }\mu\text{m}$. The collodion thin films could be used as the absorption layer materials of infrared thermal detectors because of the properties mentioned above.

2.4. Elliptical polarization measurement of collodion thin film

One-sided polishing silicon wafer is used as substrate, the collodion thin film is prepared by using spin-coater, and the spin coating speed and time are 2200 r/min and 12 s , respectively. The optical constants of collodion thin film are measured by using M-2000UI ellipsometer from J.A.WOL-LAM Company. The incident angle of elliptically polarized light is 70° . The extinction coefficient and refractive index of collodion thin film in visible light region are shown in Fig. 4.

The fitting curves of collodion thin film are showed in Fig. 5, and the thickness of collodion thin film is about 928 nm . It can be seen from Fig. 4 that the maximum refractive index is nearly 1.526 in short wave purple light and the refractive index of collodion thin film is about 1.501 in the long wave red light. In the visible light region, its extinction coefficient and refractive index decrease with the increase of wavelength, which accord with normal dispersion.

3. Micro-processing of collodion thin film

It has not been reported that the collodion thin film is etched using plasma. We attempt to etch the collodion thin

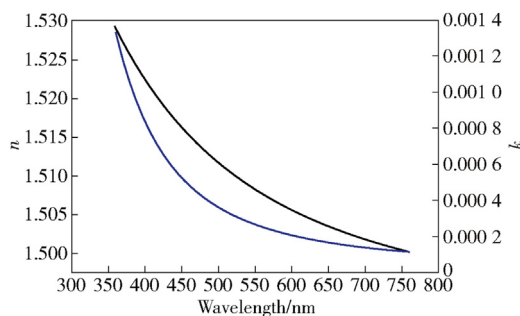
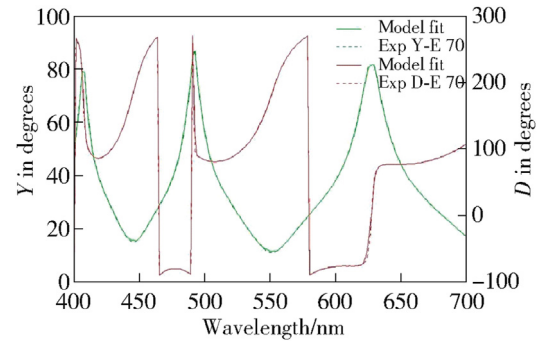
Fig. 4. n and k of collodion film.

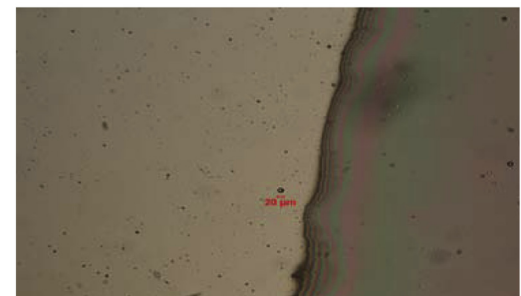
Fig 5. The fitting curves of collodion thin film.

film by oxygen gas plasma. ICP-98A high-density plasma etcher designed by Institute of Microelectronics of Chinese Academy of Sciences is used. The etching parameters are the radio frequency power of 170 W , the etching time of 3 min , the gas flow of 80 sccm and the working pressure of 2 Pa . A 2 inches one-sided polishing silicon wafer is used as substrate; the thin film sample wafer is prepared by using spin-coating technique with rotating speed of 1800 r/min and rotate time of 12 s . The sample is treated before etching, one part is covered with a mask and the rest is uncovered. The polarizing microscope pictures before and after etching are shown in Fig. 6(a) and (b). The thickness of uncovered part is measured randomly by using MP-100S, Fit value and the mean squared error (MSE) are less than 1 and the thickness of collodion thin film is listed in Table 2.

It can be seen from Fig. 6(b) that an obvious interface is between the covered part and the uncovered part, which demonstrates that the collodion thin film is etched out. In Table 2, the average thickness of collodion thin film after



(a) before etching



(b) after etching

Fig. 6. The polarizing microscope pictures of silicon surface.

Table 2
The thicknesses of collodion films before and after etching

Description	Thickness/nm
Before etching	1323
After etching	1.2

etching is about 1.2 nm. The calculated etching rate is about 7 nm/s in the terms of this technological parameter.

4. Conclusions

The spin-coating is an ideal method to prepare the collodion thin film. The collodion thin film prepared by this method has good uniformity and high repeatability. Its visible light transmittance is 91.9%, and its average infrared absorption coefficient is better than $0.69/\mu\text{m}$. Collodion film could be used as the absorption layer material of uncooled infrared detectors. It could be etched out using gas oxygen plasma. When the radio frequency power is 170 W, the etching time is 3 min, the oxygen gas flow is 80 sccm, and the working pressure is 2 Pa, the etching rate of collodion film is about 7 nm/s.

Acknowledgments

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